

THE POTENTIAL USE OF FLY ASH WITH A HIGH CONTENT OF UNBURNED CARBON IN GEOPOLYMERS

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ABSTRACT

The electric and thermal energy produced by combusting of fossil fuels – coal appears to be still dominant in a near future. Therefore, high quantities of fly ashes produced worldwide by heating and thermal power plants will even increase. In the Slovak Republic, nine tenths of fly ash is hydraulically transported to landfill areas or mines, causing ecological risks. Only a marginal part is used as a secondary raw material, mainly in the building industry. However, according to the European legislation only fly ashes with a low content of unburned coal residues, expressed by the loss on ignition (LOI), are allowed to be utilized. With the aim to alternatively use fly ashes, including those already deposited, various factors have been studied as to their influence on the compressive strength evolution of geopolymers containing untreated black coal fly ashes with a high LOI. Geopolymers with a mechanical strength of up to 55 MPa were prepared after 90 days of hardening by manipulating some crucial parameters of the activation solution and the geopolymerization mixture. An influence of the replacement of up to 20 % of fly ash by various aluminosilicate materials such as slag, kaoline, metakaoline, bolus and calcined bolus on the hardened geopolymers' mechanical properties was also analysed.

KEYWORDS: fly ashes, unburned coal residues, geopolymers, alkaline activation, mechanical strength

INTRODUCTION

Quantities of fly ashes are generated by power stations that use coal as an energy source. Only a small part of these ashes is utilized. A majority of fly ashes is hydraulically transported to settling basins or extracted mines. The deposited fly ashes, being exposed to exogenous and biogenous factors that change their chemical and structural composition, become harmful for the environment. Although fly ashes can be utilized in building industry, the European standards STN EN 206-1 limit their content of unburned coal residues to 2 – 5 % LOI (loss on ignition). Thus, only a small fraction of fly ashes produced in the Eastern Slovakia, having obviously a high content of unburned coal residues (more than 10 % LOI) can be incorporated as a secondary raw material into building materials.

It follows from the above that unburned carbon that is responsible for the loss on ignition represents an undesirable constituent of fly ashes to be utilized in the reinforced concrete construction. The problem is that the unburned carbon in fly ashes has several detrimental effects on the concrete. Especially, it

increases the electrical conductivity of the concrete, changes the color of mortar and concrete (they may appear black), etc. Moreover, the water/(cement+fly ash) ratio, needed to obtain a cement paste with a required rheological properties or consistency, is higher for fly ashes with a high carbon content, increasing the corrosivity of metallic parts incorporated in the concrete (Ha et al., 2005). Finally, it causes a poor air entrainment behavior and mixture segregation (Freeman, 1997).

A current possibility of utilizing high-LOI fly ashes is a synthesis of geopolymers. These new materials are synthetic inorganic polymers resulting from an inorganic polycondensation reaction of solid aluminosilicates in an activating solution at an elevated temperature. From the chemical point of view, geopolymers have been designated as poly(sialates), i.e. silicon-oxo-aluminates forming a network of SiO₄ and AlO₄ tetrahedra linked alternatively by sharing all oxygen atoms, based on the ability of Al ions with the 4-fold and 6-fold coordination with oxygens to induce crystallographic and chemical changes in the SiO₂ structure. They have

the empirical formula: $M_n\{-(SiO_2)_z-AlO_2\}_n \cdot wH_2O$, where M represents a cation (K^+ , Na^+ , Ca^{2+} , Ba^{2+} , NH_4^+ , H_3O^+ , ...) in voids of the polysialate structure, neutralizing the excessive negative charge of Al^{3+} in the IV-fold coordination with oxygens, n is the degree of polycondensation and z is 1, 2, or 3 (Davidovits, 1991).

Geopolymerization is the sum of several heterogeneous reactions taking place simultaneously. It can be divided into four steps: (i) dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution, (ii) formation of oligomers species (geopolymers precursors) consisting of polymeric bonds of Si–O–Si and/or Si–O–Al type, (iii) polycondensation of the oligomers to form a three-dimensional aluminosilicate framework (geopolymeric framework) and (iv) bonding of the undissolved solid particles into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure (Davidovits, 2008; Xu and Deventer, 2000; Panias, 2007).

Geopolymers exhibit excellent mechanical properties, a resistance to the corrosive solutions of sulphates and chlorides, acid solutions and a good frost resistance. Furthermore, they can withstand the exposure to temperatures of up to 600–800 °C (Škvára, 2005). Geopolymers behave similarly to zeolites; they immobilize hazardous elemental wastes within the geopolymeric matrix, acting also as a binder to convert semi-solid waste into an adhesive solid. Hazardous elements present in waste materials mixed with geopolymer compounds are 'locked' into the three dimensional framework of the geopolymeric matrix (Davidovits, 1991).

Various solid Si–Al materials (natural materials as kaoline or modified as metakaoline and also industrial wastes, e.g. coal-fired fly ashes, slag and mine tailings) can be used in the role of aluminosilicates in the geopolymerization process. Therefore, geopolymerization can be considered as an economically viable technology for the transformation of industrial wastes and/or by-products with an aluminosilicate composition into attractive construction materials. This potential application of geopolymerization has gained an increasing attention during the last decades, creating a new field for the research and technological development (Panias, 2007).

Concerning the utilization of fly ashes for the geopolymer production, their content of unburned coal residues is also important since it influences mechanical properties and binding ability of the final geopolymeric matrix. According to Jaarsveld et al. (1997, 1999), a higher LOI causes a lower final strength as well as a higher porosity of prepared geopolymers.

In general, it can be assumed that properties of (final) geopolymers depend on initial properties of used solid materials from beginning to a completion

of the hardening process. These properties can be positively influenced by separating unwanted components from the material (e.g. by the magnetic separation of Fe, corona separation or flotation of unburned coal residues), converting crystalline minerals into their analogues with an amorphous structure (kaoline – metakaoline), and also by a mechanical treatment (melting, sorting).

In this study, a few key factors influencing the synthesis of geopolymers with the fly ash-based basic aluminosilicate material (BM), manifested through the compressive strength evolution, are examined, namely the amount of Na_2O related to the BM mass and the SiO_2/Na_2O ratio (M_s modulus) in the activation solution (AS), and the curing temperature of the geopolymer mixture. A special attention will be paid to studying the role of some other solid aluminosilicate additives with different chemical and mineralogical compositions.

MATERIALS AND METHODS

FLY ASH AND OTHER ADDITIVES

Fly ash as well as other additives such as ground slag, kaoline, metakaoline, bolus and calcined bolus were applied as a basic material of geopolymers. Fly ash originating from black coal-fired melting boilers in a district heating plant in Košice at the temperature of 1400 – 1550 °C was used. Samples of the fly ash were collected from an upper layer of the coal-ash settling basin in Krásna nad Hornádom, homogenized and dried to have the 0.5 wt% water content. Subsequently, coarse impurities were removed on a sieve with 1 mm openings. No other treatment was applied to the fly ash samples.

Slag was produced in the same combustion process as the fly ash. Kaoline from two different deposits was tested: kaoline I from Rudník (LB Minerals Company, Slovakia) and kaoline II from Tomášovce (Kerko Company, Slovakia). Bolus (montmorillonized and kaolinized clay overburden of coal containing oxides and hydroxides of iron and titanium) was obtained from the middle part of Czech brown coal bush. Metakaoline and calcined bolus were prepared by calcinating of kaoline and bolus, respectively, at 750 °C for 4 hours. After drying, all the samples (except fly ash) were comminuted in a laboratory mill for 15 minutes. The grain size analysis showed that approx. 70–80 % of fly ash and ground slag particles and 100 % of ground kaoline, metakaoline and bolus particles were less than 45 µm.

A chemical and mineralogical composition of used materials is summarized in Tables 1 and 2, respectively. The phase analysis was performed using the X-ray diffractometer URD-6/ID 3003 (Rich. Seifert-FPM, Germany) under following conditions: X-ray radiation $Co K\alpha$, high voltage 40 kV, current 35 mA, step scan mode with step of $0.05^\circ 2\theta$, time per step 3 s and digital processing of output data. The manufacturer's software Rayflex X (RayfleX scanX

Table 1 Partial chemical composition of used materials.

wt. %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI	SiO ₂ /Al ₂ O ₃
Fly ash	46.77	15.69	8.34	3.93	1.21	-	-	-	23.25	2.98
Slag	57.60	23.10	9.86	3.87	1.36	0.52	2.00	0.89	0.23	2.49
Kaoline I	73.60	16.70	1.10	0.06	0.40	-	-	0.54	4.00	4.41
Kaoline II	45.46	25.95	-	-	-	-	-	-	-	1.75
Bolus	21.00	18.50	-	-	-	-	-	-	-	1.14

Table 2 Mineralogical composition of used materials.

wt. %	amorphous	hematite	kaolinite	quartz	microcline	muscovite	mullite
Fly ash	83.56 ± 2.04	1.57 ± 0.93	-	6.42 ± 0.96	-	-	8.46 ± 1.83
Slag	100.00 ± 0.00	-	-	-	-	-	-
Kaoline I	0.00 ± 10.80	-	36.80 ± 7.50	38.29 ± 2.91	11.42 ± 2.13	21.40 ± 4.50	-
Metakaoline I	19.30 ± 9.60	-	-	49.40 ± 4.50	10.90 ± 3.60	20.30 ± 6.60	-
Kaoline II	0.00 ± 12.30	-	87.60 ± 12.30	7.33 ± 0.87	14.50 ± 3.30	-	-
Metakaoline II	64.00 ± 5.40	-	-	10.87 ± 1.26	-	22.80 ± 4.80	-
Bolus	11.20 ± 7.80	12.87 ± 1.74	64.60 ± 07.20	3.84 ± 0.69	-	-	-
Calcined bolus	62.49 ± 2.97	26.93 ± 2.43	-	4.18 ± 0.63	-	-	-

Table 3 Content of SiO₂ and Al₂O₃ in the 10 M NaOH leaching solution after 24 hours.

material	Fly ash	Slag	Kaoline I	Metakaoline I	Kaoline II	Metakaoline II	Bolus	Calcined bolus
SiO₂ [mg.l⁻¹]	780	290	3920	43000	9950	15290	1700	16530
Al₂O₃ [mg.l⁻¹]	675	235	3148	7678	6385	15044	1786	14642

and RayfleX Analyze, version 2.289) was used for the measurement and data processing. The semiquantitative analysis of data was performed using the RayfleX Autoquan software, version 2.6. It represents a commercial, modified version of the program BGMN. For the chemical analysis, the atomic absorption spectroscopy (AAS) (Perkin Elmer instrument, model 1100 B) was used. The loss-on-ignition (LOI) test was used to determine the unburned carbon, especially in the fly ash sample. The sample was heated to 110 °C to drive off water. Then, it was placed in a furnace where oxidized at 815 °C. LOI is finally determined as a weight loss of the dry fly ash sample.

To determine the leachability of Al and Si from fly ash and other solid aluminosilicates (Phair, 2001), their concentrated suspensions were prepared in the 10 M NaOH alkali activator. The suspensions, containing 24 g of solid dispersed in 50 ml, were

mixed for 24 hours, centrifuged, filtered and diluted with 5 % cont. HCl before the analysis of the elemental concentrations by AAS (Table 3). The characterization of unburned coal particles is presented elsewhere (Michalíková, 2010).

ACTIVATION SOLUTION

The activation solution was prepared by mixing of solid NaOH pellets with Na-water glass and water in the ratio requested. Sodium water glass from the Kittfort Praha Co. with the density of 1.328-1.378 g/cm³ was used. It contains 36 - 38 % Na₂SiO₃ and the molar ratio of SiO₂/Na₂O is 3.2 - 3.5. Solid NaOH with the density of 2.13 g/cm³ was obtained from different producers but they all had similar chemical compositions and physical properties, containing at least 98 % of NaOH and up to 1 % of Na₂CO₃.

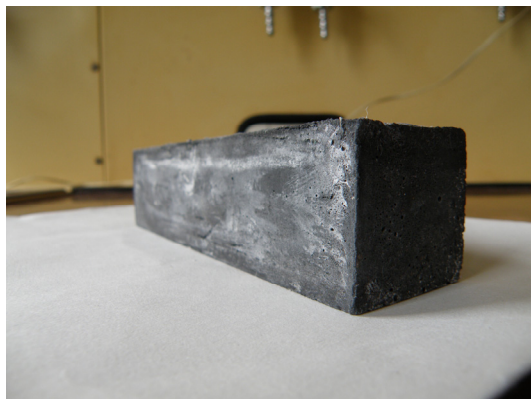


Fig. 1 A sample of hardened geopolymer immersed in the 1 % H_2SO_4 solution for 180 days. The preparation conditions: $M_s = 1.25$, $w = 0.3$. The curing time and temperature was 6 h and 80 °C, respectively.

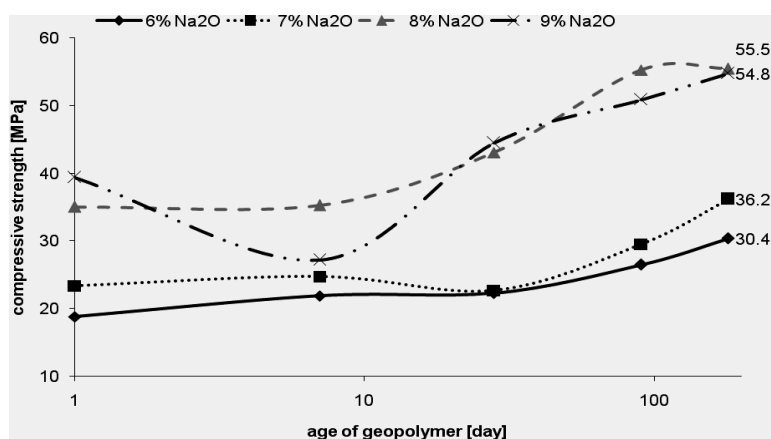


Fig. 2 Compressive strength evolution of fly ash-containing geopolymers with a different amount of Na_2O related to the fly ash mass ($\text{Na}_2\text{O}/\text{BM} \times 100$). Cured for 6 hours at 80 °C, $M_s = 1.25$, $w = 30$ % (no other additive material).

The SiO_2 -to- Na_2O ratio (M_s modulus) in the alkaline activation solution was adjusted by adding NaOH into the water glass to range from 0.75 to 1.65. The water content w was set constant at 0.3.

PREPARATION OF GEOPOLYMERS

The solid materials (BM), i.e. fly ash and additives, were combined and then dispersed in the activation solution in a selected proportion by mixing for 15 minutes. This dispersion was poured into 40x40x160 mm forms, compacted on the vibration table VSB-40 for 10 minutes at the frequency of 50 Hz and cured in a hot-air drying chamber for 6 or 12 hours at the temperature of 21, 40, 60, 80 and 100 °C. After that, the samples were removed from the forms, marked and stored in laboratory conditions until their next usage. For an illustration Figure 1 shows a sample of fly ash-based

geopolymer after its withdrawal from an aggressive solution (1 % H_2SO_4) in which it was immersed for 180 days. See the figure caption for the preparation details of the geopolymer.

The compressive strength of the hardened samples were determined after the elapse of 1, 7, 28, 90 and 180 days using the hydraulic machine Form+Test MEGA 100-200-10D.

RESULTS AND DISCUSSION

EFFECT OF THE Na_2O -TO-BASIC MATERIAL RATE

The untreated fly ash (23.3 wt% LOI) was mixed with the activation solution in a proportion (BM/AS) of 2.95, 2.90, 2.84 and 2.79 g/ml, providing the total amount of Na_2O in the solution to be 6, 7, 8 and 9 % of the fly ash mass, respectively (with M_s of the activation solution kept constant at 1.25). The water content w was always 30 %. The samples were cured

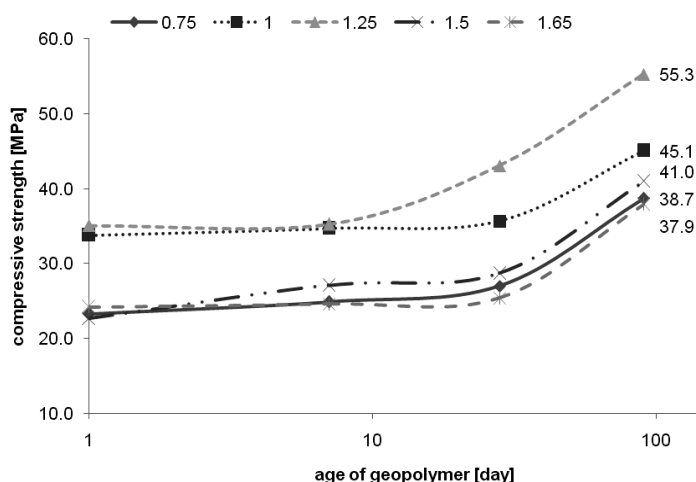


Fig. 3 Compressive strength evolution of fly ash-containing geopolymers with a different M_s ($\text{SiO}_2/\text{Na}_2\text{O}$). Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $w = 30\%$ (no other additive material).

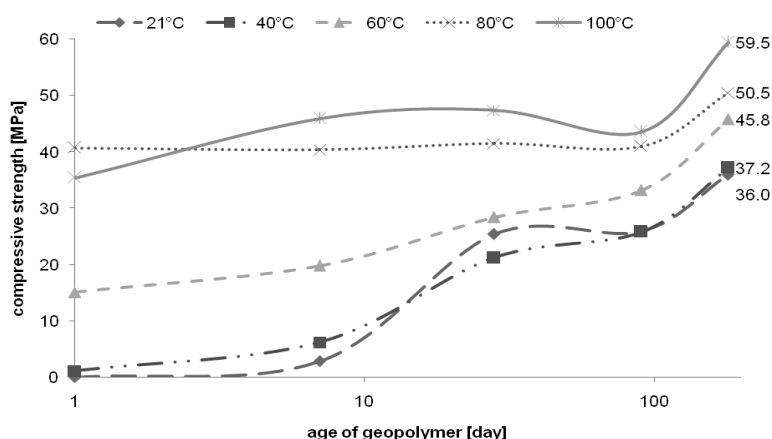


Fig. 4 Compressive strength evolution of fly ash-containing geopolymers at a different curing temperature. Cured for 12 hours, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $w = 30\%$ (no other additive material).

6 hours at 80 °C. As shown in Figure 2, the increase of Na_2O amount results in an increase of the compressive strength of the hardening geopolymers from 30.4 MPa and 36.2 MPa for 6 and 7 % Na_2O to 55.5 MPa and 54.8 MPa for 8 and 9 % Na_2O , respectively, after 180 days.

EFFECT OF THE SiO_2 -TO- Na_2O RATIO

In these experiments, mixtures were prepared at the same conditions as in the above paragraph but with the alkaline activator having M_s in the range 0.75 to 1.65 and the total Na_2O amount set at 8 wt%. Figure 3 reveals that the compressive strength of geopolymers hardened during first 90 days increases

from 38.7 MPa to 55.3 MPa for M_s increasing from 0.75 to 1.25, respectively. However, the additional increasing of M_s causes a decrease of the compressive strength to the initial value (37.9 MPa for $M_s=1.65$). Apparently, there is an optimum value of M_s at which the compressive strength is at maximum, irrespective of the hardening time.

EFFECT OF THE CURING TEMPERATURE

Figure 4 displays a compressive strength evolution of geopolymer samples prepared at analogous conditions as above (see the figure caption) but cured at the ambient (21 °C) and risen temperatures (40, 60, 80 and 100 °C) for 12 hours. It

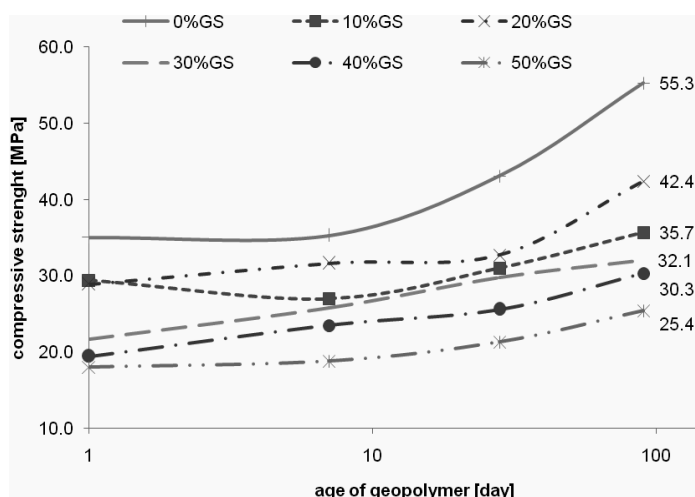


Fig. 5 Compressive strength evolution of fly ash-containing geopolymers with the addition of ground slag. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $M_s = 1.25$, $w = 30\%$.

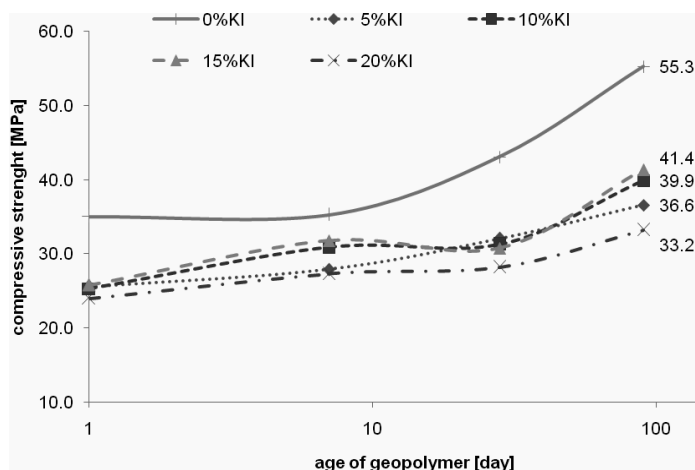


Fig. 6 Compressive strength evolution of fly ash-containing geopolymers with the addition of kaoline I. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $M_s = 1.25$, $w = 30\%$.

is visible that the samples cured at lower temperatures (21, 40 and 60 °C) manifest a step-like evolution of strength with time. For all curing temperatures, after the initial increase within 28 days of strenghtening, a plateau is observable for the next time period between 28 and 90 days. A second rise appears when the time of hardening further proceeds above 90 days. Also, an increase in the curing temperature stimulates a continuous increase in the strength.

EFFECT OF ADDITIVES

The mixtures were prepared by replacing a part (5 – 50 %) of fly ash with ground slag (GS), kaoline I (KI), kaoline II (KII), metakaoline I (MKI),

metakaoline II (MKII), bolus (B) and calcined bolus (CB) at the BM/AS ratio = 2.84 g/ml, $M_s = 1.25$, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\text{ wt}\%$, the content of water 30 %, and at the curing temperature = 80 °C (6 hours).

A few facts follow from Figures 5 to 11, presenting the evolution of mechanical properties of geopolymers with the additives: First, the compressive strength of geopolymers with up to 10 % of additives is, in the whole course of the hardening process, lower than that for geopolymers prepared only from fly ashes; an exception is the geopolymer in which fly ash is combined with calcined bolus, exhibiting a higher strength after 7 days but not after 90 days (see Fig. 12, summarizing the values of the compression strength

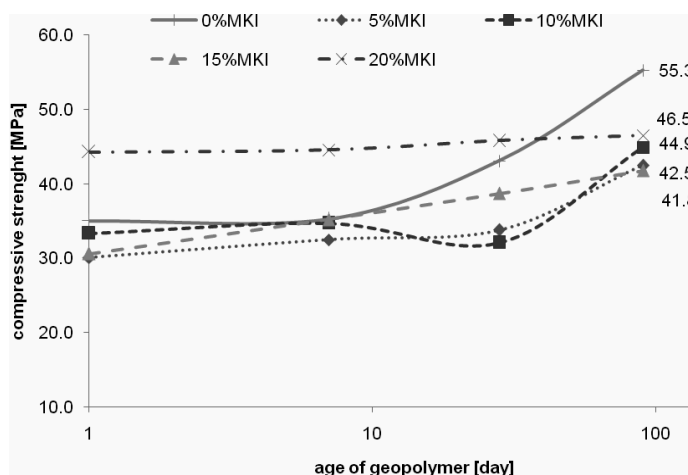


Fig. 7 Compressive strength evolution of fly ash-containing geopolymers with the addition of metakaoline I. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8 \%$, $M_s = 1.25$, $w = 30 \%$.

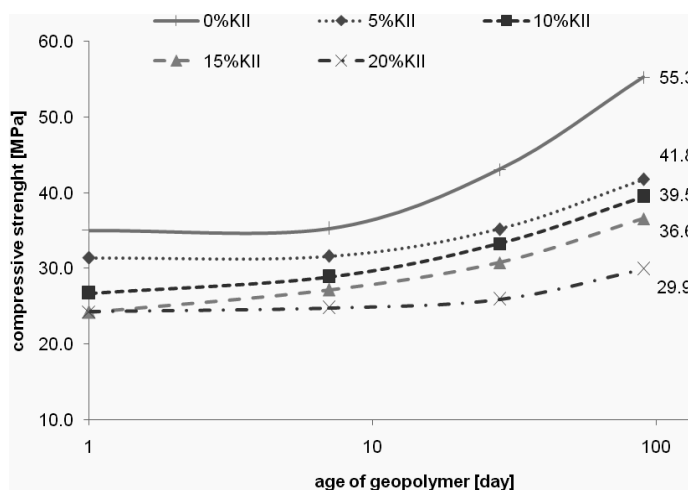


Fig. 8 Compressive strength evolution of fly ash-containing geopolymers with the addition of kaoline II. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8 \%$, $M_s = 1.25$, $w = 30 \%$.

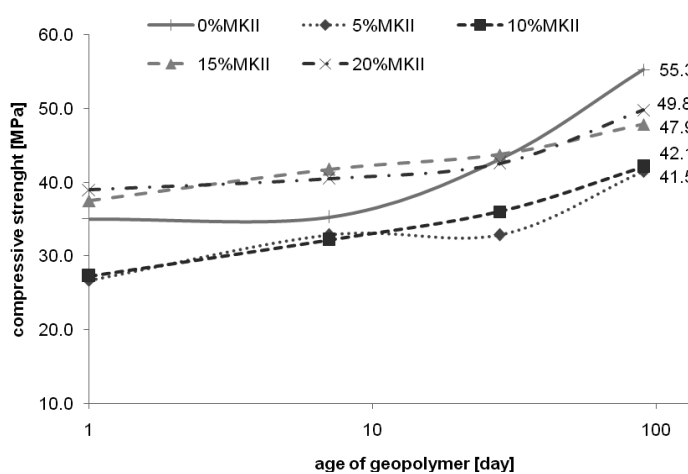


Fig. 9 Compressive strength evolution of fly ash-containing geopolymers with the addition of metakaoline II. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8 \%$, $M_s = 1.25$, $w = 30 \%$.

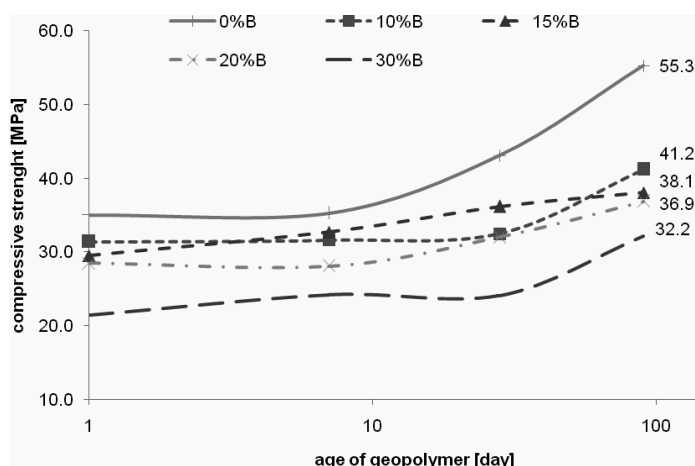


Fig. 10 Compressive strength evolution of fly ash-containing geopolymers with the addition of bolus. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $M_s = 1.25$, $w = 30\%$.

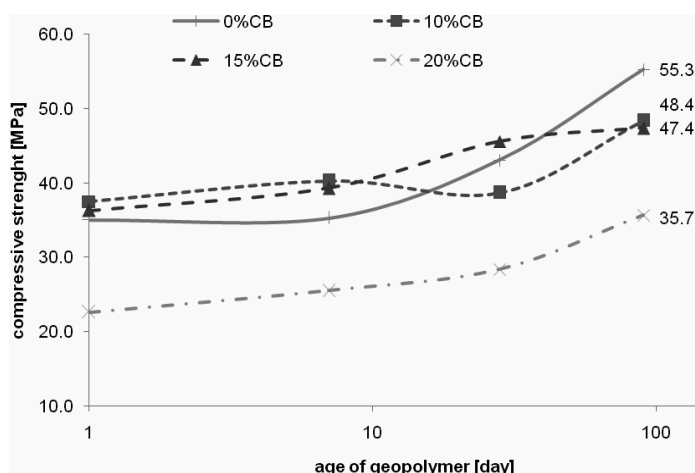


Fig. 11 Compressive strength evolution of fly ash-containing geopolymers with the addition of calcined bolus. Cured for 6 hours at 80 °C, $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $M_s = 1.25$, $w = 30\%$.

of geopolymers with 10 % additives after 7 and 90 days, left and right columns, respectively). Second, when the content of additives is above 10 %, say 20 % (Fig. 13), geopolymers with both metakaolines manifest higher strengths after 7 days, as related to that for the fly ash geopolymer, whereas after 90 days the strengths are again lower. The strength of geopolymers with another additives is even lower (it concerns both the 7 and 90 days strengths), including the calcined bolus. A further increase of the fly ash replacement for additives would deepen the above trends. For example, the compressive strength of the 90-days geopolymer prepared only with fly ash was

55.3 MPa but fell to 25.4 MPa when 50 % of fly ash was replaced by slag (Fig. 5).

CONCLUSION

The article presents results of preliminary laboratory tests on the compression strength evolution of geopolymers containing fly ash with a high amount of unburned coal residues (23.25 wt% loss on ignition), taken from a settling basin where it was exposed to atmospheric influences and erosion for a long time (2 – 5 years). It has been found that geopolymers with a mechanical strength of up to 55 MPa after 90 days of hardening can be prepared by

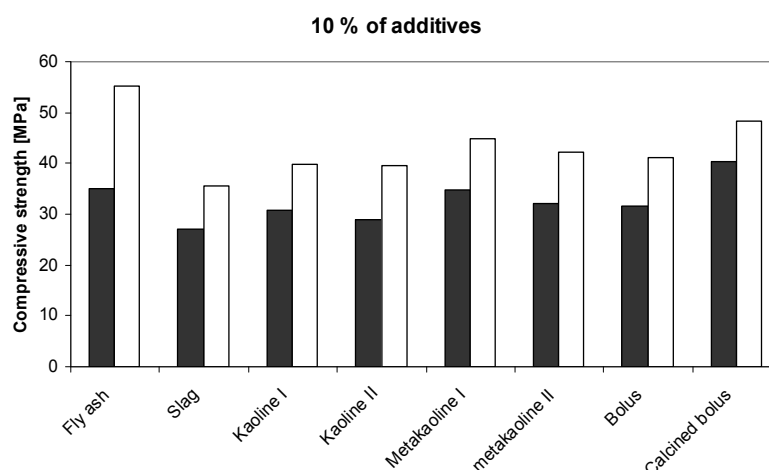


Fig. 12 Compressive strength of geopolymers with fly ash replaced by 10 % of other additives. Measured after 7 and 28 days (black and white columns, respectively).

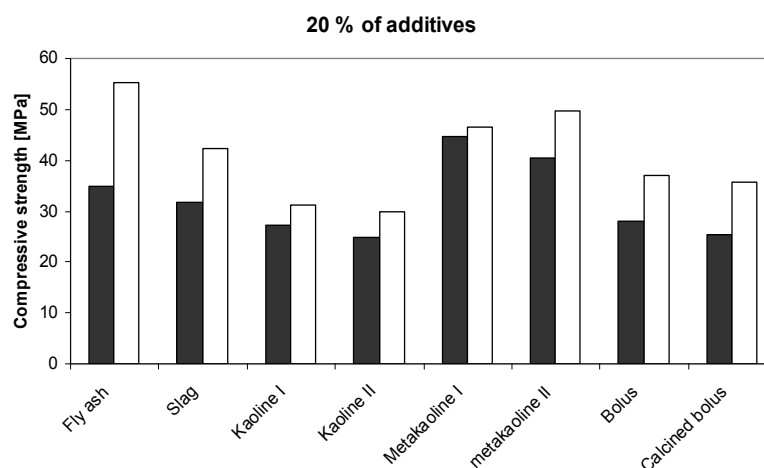


Fig. 13 Compressive strength of geopolymers with fly ash replaced by 20 % of other additives. Measured after 7 and 28 days (black and white columns, respectively).

manipulating some crucial parameters of the activation solution and the geopolymerization mixture. A replacement of up to 20 % of fly ash by various aluminosilicate materials is not so beneficial to the hardened geopolymers' mechanical properties as thought previously.

Nevertheless, the addition of metakaolines increases the compressive strength during the initial stage of the geopolymerization process. Interestingly, the extraordinary effect is comparable for both metakaolines despite of the fact that the chemistry of kaolines (e.g. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio being 4.41 vs. 1.75 for kaoline I and II, respectively, see Table 1) as well as mineralogy of metakaolines (e.g. amorphousness being 19.3 and 64.0 for metakaoline I and II,

respectively, see Table 2) are very different. Both the metakaolines also differ in their leachability (Table 3). On the other hand, the impact of calcined bolus is special in that the 10 % addition fastens the early stage of geopolymerization reaction (as the only from among all the studied additives) but this effects is lost when the addition increases to 20 %), although the percentages of amorphous phase (64.0 and 62.5, respectively) as well as leaching of metakaoline II and calcined bolus are almost identical (quite high). Finally, slag with its 100 % amorphousness but a minimal leaching ability has an intermediate effect to the mechanical strength of fly ash based geopolymers.

It can be concluded that neither the chemical nor the mineralogical composition alone of solid aluminosilicates are decisive as to the prediction of their influence on the properties of geopolymers. It seems that surface physico-chemical parameters should be studied in conjunction with bulk chemical and phase characteristics of solids in order to evaluate the role of aluminosilicate precursors in the geopolymerization reaction satisfactorily and to prepare geopolymer materials with required properties.

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REFERENCES

- Davidovits, J.: 1991, Geopolymers: Inorganic polymeric new materials, in *Thermal Analysis*, 37, 1633–1656.
- Davidovits, J.: 2008, Geopolymer: Chemistry and applications, Institut Géopolymère, France.
- Freeman, E., Gao, Y.-M., Hurt, R. and Suuberg, E.: 1997, Interactions of carbon-containing fly ash with commercial air-entraining admixtures for concrete, *Fuel*, 76, no. 8, 761–765.
- Ha, T.H., Muralidharan, S., Bae, J.H., Ha, Y.C., Lee, H.G., Park, K.W. and Kim, D.K.: 2005, Effect of unburnt carbon on the corrosion performance of fly ash cement mortar, *Construction and Building Materials*, 19, 509–515.
- Michalíková, F., Škvarla, J., Krinická, I., Sisol, M. and Kolesárová, M.: 2010, The contribution to the petrology of unburned coal residues from combustion of black coal in thermal power plants, 14th Conference on Environment and mineral processing, part II, 285–290.
- Palomo, A., Grutzeck, M.V. and Blanco, M.T.: 1999, Alkali-activated fly ashes, a cement for the future, *Cement and Concrete Research*, 29 (8), 1323–1329.
- Panias, D., Giannopoulou, I.P. and Perraki, T.: 2007, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301, 246–254.
- Phair, J.W. and van Deventer, J.S.J.: 2001, Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers, *Minerals Engineering*, 14, no. 3, 289–304.
- Škvára, F., Jílek, T. and Kopecký, L.: 2005, Geopolymer materials based on fly ash, *Ceramics - Silikáty*, 49, 195–204.
- van Jaarsveld, J.G.S.: 1997, The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications, *Minerals Engineering*, 10, no. 7, 659–669.
- van Jaarsveld, J.G.S., van Deventer, J.S.J. and Schwartzman, A.: 1999, The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics, *Minerals Engineering*, 12, no. 2, 75–91.
- Xu H. and van Deventer, J.S.J.: 2000, The geopolymerisation of alumino-silicate minerals, *International Journal of Mineral processing*, 59, 247–266.